A global inventory of stratospheric chlorine in 2004 based on measurements by the Atmospheric Chemistry Experiment Fourier Transform Spectrometer (ACE-FTS)

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Abstract

Total chlorine (Cl_{TOT}) in the stratosphere has been determined using the Atmospheric Chemistry Experiment Fourier Transform Spectrometer (ACE-FTS) measurements of HCl, ClO, $ClONO_2$, CH_3Cl, CCl_4, CCl_3F (CFC-11), CCl_2F_2 (CFC-12), $CHClF_2$ (HCFC-22), CCl_2FCClF_2 (CFC-113), and CH_3CClF_2 (HCFC-142b), supplemented by $CHClF_2$, ClO, ClOOCl, HOCl, COClF, $COCl_2$, and CH_3CCl_3 data from other sources including both measurements and models. Separate chlorine budgets were determined for the northern high latitudes (60-82ºN), northern midlatitudes (30-60ºN), the tropics (30ºS-30ºN), southern midlatitudes (30-60ºN) and southern high latitudes (60-82ºS). The period of February 2004 - January 2005 inclusive was averaged when possible, to deal with seasonal variations. Diurnal variation was avoided by only using measurements taken at local sunset. We obtained mean stratospheric Cl_{TOT} values of 3.62 ± 0.10 ppbv for both the northern and southern midlatitudes independently, with a slightly lower value in the tropics and slightly higher values at high latitudes. Stratospheric Cl_{TOT} profiles in all five latitude ranges are nearly linear with a slight positive slope in ppbv/km. We interpret both the observed slope and pattern of latitudinal variation as evidence of the beginning of a decline in global stratospheric chlorine, which is qualitatively consistent with the mean stratospheric circulation pattern and time lag necessary for transport.

1. Introduction

Since the discovery of large ozone losses over Antarctica by *Farman et al.* [1985] as well as evidence of ozone depletion over the Arctic and more populated areas at lower latitudes, stratospheric ozone depletion has been recognized as a problem warranting serious scientific investigation. The majority of ozone loss is related to the anthropogenic emission of organic chlorine and bromine compounds. The principal organic chlorine compounds including chlorofluorcarbons (CFCs), hydrochlorofluorocarbons (HCFCs), halons, carbon tetrachloride (CCl_4), and methyl chloroform (CH_3CCl_3) are chemically very stable in the troposphere where they behave as greenhouse gases, contributing to global climate change. These long-lived compounds are eventually transported to the stratosphere where they are photolysed by UV radiation, or broken down by reaction with radicals such as $O(^1D)$, OH and Cl. As a result, chlorine monoxide (ClO) is formed which can destroy ozone via the catalytic cycle [*Molina and Rowland*, 1974]:

$$ClO + O \rightarrow Cl + O_2 \quad (1.1)$$
$$Cl + O_3 \rightarrow ClO + O_2 \quad (1.2)$$
$$\text{Net: } O + O_3 \rightarrow 2O_2 \quad (1.3)$$

In the polar regions, the modified catalytic cycle [*Molina and Molina*, 1987] which does not require oxygen atoms is the dominant cause of ozone destruction:

$$2\,(Cl + O_3 \rightarrow ClO + O_2) \quad (2.1)$$
$$ClO + ClO \rightarrow ClOOCl \quad (2.2)$$
$$ClOOCl + h\nu \rightarrow Cl + ClOO \quad (2.3)$$
$$ClOO + M \rightarrow Cl + O_2 + M \quad (2.4)$$
$$\text{Net: } 2O_3 \rightarrow 3O_2 \quad (2.5)$$

Additionally, cycles involving chlorine and other species such as bromine compounds are also of importance:

$$ClO + BrO \rightarrow Br + Cl + O_2 \quad (3.1)$$
$$Cl + O_3 \rightarrow ClO + O_2 \quad (3.2)$$
$$Br + O_3 \rightarrow BrO + O_2 \quad (3.3)$$
$$\text{Net: } 2O_3 \rightarrow 3O_2 \quad (3.4)$$

Each of these catalytic cycles repeats numerous times before undergoing an alternate pathway leading to conversion to a reservoir compound such as chlorine nitrate ($ClONO_2$) or hydrogen chloride (HCl). However, heterogeneous reactions on the surface of polar stratospheric clouds (PSCs) can cause temporary chlorine reservoir species such as $ClONO_2$ and HCl to react, forming active chlorine ClO_x = Cl, ClO, and ClOOCl, and enabling the catalytic destruction of ozone.

At midlatitudes, destruction of ozone by ClO_x occurs at altitudes encompassing the stratosphere but has the largest impact in the lower and middle stratosphere, with peak

destruction near 40 km altitude. Above about 45 km, ClO_x reactions still occur, but the Chapman cycle [*Chapman*, 1930] and catalytic cycles involving HO_x are the dominant causes of ozone loss, whereas in the lower stratosphere, the NO_x and HO_x cycles are most important [*World Meteorological Organization (WMO)*, 1999 (chapter 6)]. BrO_x species which undergo a catalytic cycle in conjunction with ClO_x, are responsible for some ozone depletion but exist at levels an order of magnitude less than ClO_x. Since the Chapman, HO_x and NO_x cycles together, naturally maintained a constant level of ozone for many decades, and BrO_x concentrations are so low, the ClO_x cycles are considered the primary cause of stratospheric ozone decline because the increase in chlorine containing compounds in the stratosphere is the result of anthropogenic emissions.

The "Montreal Protocol on Substances that Deplete the Ozone Layer" is a treaty adopted in 1987 by the international community to control the emission of substances that contribute to ozone depletion. It has been strengthened further in later years through numerous amendments. Essentially all of the most destructive ozone depleting substances such as CCl_4, CH_3CCl_3, CFCs and halons are now banned under the Montreal Protocol and its amendments. The banned compounds were largely replaced by HCFCs which typically have shorter tropospheric lifetimes and lower ozone depleting potentials (ODPs) than CFCs, although these are also being phased out and replaced with hydrofluorocarbons (HFCs) which do not contain chlorine.

Prior to the widespread use of these ozone depleting gases only a few decades ago, total stratospheric chlorine had a value equal to the natural background level of about 0.6 ppbv (parts per billion by volume) primarily due to CH_3Cl. Observations indicate that mean stratospheric Cl_{TOT} reached 3.70±0.20 ppbv around 1997 [*Sen et al.*, 1999] and has recently begun a slow decline [*Anderson et al.*, 2000; *Mahieu et al.*, 2004] as a result of the emission restrictions required by the Montreal Protocol and its amendments, but the exact date and the volume mixing ratio (VMR) of the maximum in stratospheric Cl_{TOT} are somewhat ill-defined [*Waugh et al.*, 2001]. Most modeling studies predict that global stratospheric ozone should fully recover shortly after stratospheric chlorine declines to 2.0 ppbv, which is expected to occur around the year 2060 [*Brasseur et al.*, 1999 (p320-321); WMO, 1999; *Prather et al.*, 1990, 1996]. However, until this happens, it is necessary to monitor polar stratospheric ozone levels and make continual measurements of the species that contribute to stratospheric chlorine. Some studies [*Austin et al.*, 1992; *Shindell et al.*, 1998] suggest that in the future, the convergence of multiple factors such as decreased stratospheric temperatures related to climate change and increased levels of stratospheric water (which have been measured in recent years, although not fully understood [*Oltmans et al.*, 2000; *Rosenlof et al.*, 2001; *Nedoluha et al.*, 2003; *Nassar et al.*, 2005a]) would lead to elevated levels of PSCs. This indicates that unless climate change and stratospheric chlorine are controlled simultaneously, the recovery of the Antarctic ozone layer could be delayed and the possibility of a future Arctic ozone 'hole' can not be completely ruled out [*Austin et al.*, 1992; *Shindell et al.*, 1998; *Shindell and Grewe*, 2001]. In a comparison of a number of chemistry-climate models carried out by *Austin et al.* [2002], most models did not predict a future Arctic ozone 'hole', but the larger range of predicted Arctic ozone scenarios in comparison to the Antarctic, highlights the difficulty in predicting the evolution of Arctic ozone with current models.

There are currently a variety of different instruments being used to measure chlorinated species in the atmosphere using in situ techniques from the ground or aircraft, or remote sensing methods from the ground, aircraft, balloons or space-based platforms. *Zander et al.* [1992, 1996] determined mean stratospheric Cl_{TOT} values of 2.58±0.10 ppbv in 1985 and 3.53±0.10 ppbv in 1994 for northern hemisphere midlatitudes, primarily using measurements from the Atmospheric Trace Molecule Spectroscopy (ATMOS) instrument which flew four times on the NASA Space Shuttle (1985, 1992, 1993 and 1994). Similarly, a value of 3.70±0.20 ppbv was determined based on measurements by the balloon-borne MkIV interferometer during the Arctic summer of 1997 [*Sen et al.*, 1999]. Both of these instruments are high-resolution infrared Fourier transform spectrometers (FTSs) which are capable of measuring a large number of chlorinated species. The determination of total chlorine from their measurements was made by summing the chlorine contributions from all significant individual species averaged over a range of stratospheric altitudes. *Zander et al.* [1992, 1996] also showed that at the top of the stratosphere (or about 50 km) nearly all of the chlorine is found as HCl.

The Halogen Occultation Experiment (HALOE) on the Upper Atmosphere Research Satellite (UARS) has produced a record of Cl_{TOT} from 1991 to 2005 based on measured values of HCl at 55 km [*Russell et al.*, 1996b; *Anderson et al.*, 2000]. According to the HALOE method, the ratio HCl/Cl_{TOT} is 0.93 at the equator and 0.95 at high latitudes, so measurements of HCl at a given latitude are divided by this ratio to obtain Cl_{TOT}. *Russell et al.* [1996b] state that HCl/Cl_{TOT} is less than 1.00 mostly due to $CHClF_2$ (HCFC-22) which has a stratospheric lifetime of over 200 years [*Weisenstein et al.*, 1992], making it the only organic chlorine compound known to exist in the upper stratosphere in significant amounts [*Weisenstein et al.*, 1992; *Rummukainen et al.*, 1996; *Coheur et al.*, 2003]. HALOE determined Cl_{TOT} values of 3.3±0.33 ppbv in June 1995 [*Russell et al.*, 1996b] and over 3.5 ppbv in 2000 [*Anderson et al.*, 2000] which indicate that HALOE Cl_{TOT} are lower than those determined by ATMOS or MkIV at a similar time.

Although ground-based measurements provide less global coverage than satellites, a large number of sites make measurements of chlorine species, which together make an important contribution to assessing chlorine levels in the atmosphere. Two of the most important sets of ground-based measurements are the Network for the Detection of Stratospheric Change (NDSC) measurements [*Rinsland et al.*, 2003] and the ALE/GAGE/AGAGE measurements [*Prinn et al.*, 2000]. The NDSC performs routine solar absorption measurements using high spectral resolution ground-based Fourier transform infrared (FTIR) spectrometers, to infer total column amounts of a number of species, including HCl and $ClONO_2$. The measurements for these two species, which date back to at least 1997 for seven northern hemisphere sites and two southern hemisphere sites in the network [Rinsland et al., 2003], can be used as an estimate of total inorganic chlorine (Cl_y) in the lower stratosphere, where HCl and $ClONO_2$ are the major contributors. The measurements up to 2001 provide evidence for stabilization in total chlorine loading, observed as a broad peak following a rapid buildup during the 1980s. An update to the NDSC time series using measurements extending through 2003, indicate that the total stratospheric inorganic chlorine loading (Cl_y) has decreased very slowly (-0.7 ±0.3%/yr, 1σ) since it peaked in late 1996 [*Mahieu et al.*, 2004].

The Atmospheric Lifetime Experiment (ALE), the Global Atmospheric Gases Experiment (GAGE), and the Advanced Global Atmospheric Gases Experiment (AGAGE) make ground based in situ measurements of both natural and anthropogenic gases important for studies of ozone depletion and climate change [*Prinn et al.*, 2000]. ALE began in 1978, but was replaced by GAGE in the 1981-1985 time frame and then by AGAGE in the 1991-1993 time frame, as technological improvements in gas chromatography (GC) became available. A prime objective of the ongoing project is the determination of the rates of emission and/or chemical destruction of CCl_3F, CCl_2F_2, CCl_2FCClF_2, CH_3CCl_3, CCl_4, $CHClF_2$, CH_2FCF_3, CH_3CClF_2, CH_3CCl_2F, $CBrF_3$ (Halon-1301), and $CBrClF_2$ (Halon-1211) from five geographically dispersed stations. ALE/GAGE/AGAGE measurements up to 1998 show either stabilization or decline for most individual source gases with $CHClF_2$ being the main exception. The Lower Tropospheric Chlorine Loading (LTCL) is calculated based on ALE/GAGE/AGAGE measurements of CCl_3F, CCl_2F_2, CCl_2FCClF_2, CCl_4, CH_3CCl_3, $CHClF_2$ and literature values for CH_3Cl and CH_2Cl_2 which are assumed to exhibit no long-term trends. The findings indicate that LTCL reached a maximum value of 3.6 ppbv and is decreasing slowly, largely driven by declines in CH_3CCl_3 and CCl_4 [*Prinn et al.*, 2000].

It is necessary to compare global satellite measurements, ground-based measurements, and industry-reported levels of source gas production and emission, with modeling studies of chemistry and transport to obtain a complete understanding of the effect of these source gases on stratospheric ozone and to make accurate predictions regarding the time frame required for ozone recovery. In the present work, we calculate stratospheric Cl_{TOT} by taking the sum of VMR profiles from all significant individual chlorine species measured by the Atmospheric Chemistry Experiment Fourier Transform Spectrometer (ACE-FTS). These data are supplemented by profiles of species measured by other instruments or in some cases calculated profiles. The sums are averaged over the entire range of stratospheric altitudes to obtain a value for mean stratospheric Cl_{TOT}, as in *Zander et al*. [1992, 1996]. We have determined separate daytime chlorine budgets for the northern high latitudes (60-82ºN), northern midlatitudes (30-60ºN), the tropics (30ºS-30ºN), southern midlatitudes (30-60ºN) and southern high latitudes (60-82ºS) within the period of February 2004 - January 2005 inclusive. The results of this global inventory of stratospheric chlorine can be used to check the validity of the high altitude HCl method of determining total chlorine, for a comparison with reported emission inventories, for assessing the effectiveness of the Montreal Protocol and for incorporating into models to predict the eventual date of recovery of the stratospheric ozone layer.

2. The ACE mission and the ACE-FTS instrument

The Atmospheric Chemistry Experiment (ACE), also known as SCISAT-1 is a Canadian satellite that was launched by NASA on 12 August 2003. The ACE instruments make solar occultation measurements during up to 15 sunrises and 15 sunsets per day from a 74º inclination circular orbit at an altitude of ~650 km. The ACE orbit was chosen to optimize occultation opportunities over midlatitude and polar regions, with the primary objective of investigating processes related to ozone depletion during the polar springtime. The primary instrument on SCISAT-1 is the ACE-FTS, a high resolution Fourier transform spectrometer operating in the 750-4400 cm^{-1} range. During each occultation, the ACE-FTS can measure

spectra at a series of tangent heights, which are subsequently inverted to give profiles of temperature, pressure, and molecular VMRs with a vertical resolution of 3-4 km. The inversion process first requires the retrieval of temperature and pressure by fitting measured CO_2 spectral lines to calculated spectral lines from a forward model, in multiple narrow spectral regions (microwindows). After retrieving temperature and pressure, VMR profiles for numerous molecules are retrieved in a similar manner, with the temperature and pressure fixed. An overview of the ACE mission is given in *Bernath et al.* [2005] and a description of ACE-FTS retrievals is given in *Boone et al.* [2005].

3. ACE-FTS Method for the determination of Total Stratospheric Chlorine

The method for determination of stratospheric Cl_{TOT} in this work is similar to the method of *Zander et al.* [1992, 1996] based on the sum of all significant chlorine species in the stratosphere. In the present work, Cl_{TOT} as a function of altitude was determined using the following summation:

$$Cl_{TOT} = [HCl] + [ClONO_2] + [ClO] + 2[ClOOCl] + [HOCl] + [COClF] + 2[COCl_2] + CCl_y \quad (4.2)$$

$$CCl_y = 4[CCl_4] + 3[CCl_3F] + 2[CCl_2F_2] + [CH_3Cl] + 3[CH_3CCl_3] + [CHClF_2] + 3[CCl_2FCClF_2] + [CH_3CClF_2] + \textit{minor species} \quad (4.3)$$

In the above equations, all organic chlorine species are grouped together as CCl_y. Figure 1 shows an example of the component profiles of CCl_y at southern midlatitudes. The above species were measured by the ACE-FTS, with the exception of those shown in italics which are based on data from other sources including measurements and models. ClO has some contribution from ACE-FTS data but is mostly based on measurements by the SMR instrument as described in section 3.2. $CHCl_2F$ is primarily based on ACE-FTS data with a modeled contribution at high altitudes as described in section 3.6. ACE-FTS retrieved VMR profiles are not constrained by the a priori, however, above the retrieval range, the a priori profile is scaled based on the values retrieved at the two highest points [*Boone et al.*, 2005]. If a reliable a priori was not available, a tail was assumed for profiles that would otherwise end abruptly in order to smoothly bring the profile to zero at the upper altitude end.

3.1 Chlorinated species retrieved from ACE-FTS spectra

Profiles of hydrogen chloride (HCl), chlorine nitrate ($ClONO_2$), methyl chloride (CH_3Cl), CFC-11 (CCl_3F), and CFC-12 (CCl_2F_2) were taken from ACE-FTS version 2.2 data which is provided on a vertical 1-km grid. CFC-113 (CCl_2FClF_2), HCFC-142b (CH_3CClF_2) and carbon tetrachloride (CCl_4) were specially retrieved for this work. HCFC-22 ($CHClF_2$) and chlorine monoxide (ClO) were partially taken from version 2.2 but supplemented with other data as described later. The altitude ranges of the microwindows used for all ACE-FTS retrieved chlorine species and the acceptable altitude range used to determine the ACE-FTS average profiles are shown in Table 1. In many cases, the spectral contribution from known interfering species including O_3, CH_4, H_2O, HDO and others were removed during retrieval.

HCl is the dominant chlorine species at high altitudes, representing about 97-98% of total chlorine at 55 km. At low altitudes, a combination of CCl_y species dominates with the largest contributions from CCl_3F, CCl_2F_2 and CH_3Cl (the only significant natural source of organic chlorine). The ACE-FTS CCl_2FClF_2 and CH_3CClF_2 profiles used in this work are the first ever retrievals of these two species from space [*Dufour et al.*, 2005].

The profile of $ClONO_2$ approximates a normal distribution with a peak ranging from 23.5 km at southern high latitudes to 28.5 km in the tropics. At its peak, $ClONO_2$ typically accounts for ~25% of the chlorine budget. ClO has a single peak in the upper stratosphere for most seasons and latitudes but is enhanced in the winter polar vortices causing a second highly-variable peak in the lower stratosphere. Since profiles of $ClONO_2$ and ClO exhibit diurnal variation, day and night profiles should not be averaged together, especially if these species are not necessarily measured at coincident locations and times. Using the longitude (λ, ranging from -180 to +180) and universal time (UT) in hours for the reference tangent point of each occultation, the local times (LT) were determined using:

$$LT = UT + (24/360)\,\lambda \qquad (5.1)$$

The above equation gives the LT relative to the stated UT calendar day, so 24 hours were added or subtracted accordingly (to values less than zero or greater than 24) to determine the standard local time (SLT) relative to the diurnal cycle. It should be noted that although all ACE occultations are labeled as sunrise or sunset as seen from orbit, outside of the tropics this label is not necessarily indicative of whether it is sunrise or sunset at the measurement location. Sorting the occultations by SLT, shows that all ACE measurements occurred at twilight and could be divided into two groups: sunrises before local noon and sunsets after local noon. For this chlorine inventory, we have taken only daytime profiles measured at local sunset, thus facilitating direct comparison to the ATMOS chlorine budgets [*Zander et al.*, 1992, 1996].

Table 2 lists the number of ACE-FTS profiles averaged for each latitude range, however, profiles with an unphysical shape were discarded as outliers, so the actual number for a given species is typically lower. In addition, some profiles are also missing one or more points at the upper and/or lower end of the altitude ranges in Table 1, as a result of variation in the tangent heights of ACE-FTS measurements prior to interpolation to the standard grid [*Boone et al.*, 2005]. We have averaged over approximately the first year of ACE-FTS measurements, February 2004 - January 2005 inclusive, to obtain our best determination of 2004 values. One full year of data was included in our averaged profiles as an attempt to account for seasonal variations, however, the limited coverage provided by the ACE orbit often results in periods of more than a month where no measurements are made for some latitudes ranges.

3.2 ClO

Since the signal-to-noise ratio (SNR) for ClO in ACE-FTS spectra is usually very low, most of the ClO measurements used in this work are from the Sub-Millimeter Receiver (SMR) [*Urban et al.*, 2005] on the Odin satellite [*Murtagh et al.*, 2002] just as *Zander et al.* [1996]

used ClO measurements from the Millimeter-wave Atmospheric Sounder (MAS) [*Hartmanm et al.*, 1996; *Aellig et al.*, 1996] for the ATMOS chlorine budget. We obtained version 1.2 SMR ClO profiles for the period of February 2004 - January 2005 inclusive, to match the temporal range of the ACE-FTS measurements. From the SMR dataset, we took only measurements with a solar zenith angle between 88-92º and only those measurements made during local sunset. The latitudes for the SMR data were selected to match the ACE-FTS average latitudes in the five latitude regions, 71±2º for high latitudes, 45±1º for midlatitudes and 15±2º for the tropics (assuming symmetry about the equator). Since all ACE-FTS southern high latitude daytime measurements occurred during the southern hemisphere winter months, SMR ClO profiles were selected for this date range rather than using data with full seasonal coverage.

The SMR profiles were interpolated to the ACE-FTS 1-km grid using a built-in spline function in Matlab®, then averaged in each latitude range. The number of SMR profiles included in each average is shown in Table 2. Profiles with unphysical shapes were discarded, as was done with the ACE-FTS data. In a few cases, an unphysical increase in SMR ClO profiles above 51.5 km was manually removed, but this is above the range of altitude considered in the calculation of stratospheric $Cl_{TOT.}$ This lower mesospheric increase has recently been identified as an artifact in version 1.2 of the SMR data and has apparently been corrected for SMR version 2.0 data (D.P. Murtagh, private communication).

At southern high latitudes in the 12.5-24.5 km range, strong ClO enhancement was measured by the ACE-FTS. Since lower stratospheric ClO enhancement is extremely variable, these measurements have been used so that the ClO profiles are properly matched to those of other species. The ACE-FTS ClO retrievals are somewhat noisy but averaging 119 southern high latitude profiles produced a smooth result. Weak ClO enhancement is observed for northern high latitudes, but the SNR is still low so the SMR profiles are used rather than ACE-FTS measurements in this altitude range.

3.3 HOCl

Attempts to retrieve HOCl from ACE-FTS spectra are in progress, however, *von Clarmann et al.* [2005] have developed a method for retrieving HOCl from MIPAS spectra, so we use these profiles as the basis for the HOCl profiles in our chorine inventory. Their work indicated that HOCl also exhibits a small diurnal variation and because our measurements are at sunset, we have taken a day-night average of the profiles shown in Figure 4 of that paper. It was necessary to manually extrapolate the upper end of their profiles to 54 km to obtain a smooth transition to zero since the profiles abruptly end at 50 km.

The work of *von Clarmann et al.* [2005] indicated a latitudinal variation in HOCl with the altitude of the maximum 2.2±0.3 km lower for the 45ºN-45ºS latitude range than for the more poleward latitudes of 45-90º in each hemisphere. This is a 2.2 km shift for a 45º change in average latitude (22.5º to 67.5º), i.e. 0.244 km per 5º or 0.0488 km per degree. Assuming hemispheric symmetry, we would expect the peak to occur at 35.0 km for the tropics (0-30ºS and 0-30ºN, average latitude 15º), at about 36.5 km for midlatitudes (30-60º, average latitude 45º) and at about 37.7 km for high latitudes (60-82º, average latitude 71º).

The HOCl zonal mean VMRs shown in Figure 3 of *von Clarmann et al.* [2005], illustrate the latitudinal variability in both the maximum VMR and the value that at which it occurs. Therefore, to account for this latitudinal variability, we estimate a scale factor and a shift to apply to the mean (day-night) 30ºN profile. We apply a scale factor of 1 and no shift for the tropics, therefore the maximum of 0.222 ppbv remains at 35.5 km for the tropics. We multiply by a scale factor of 0.895 and apply a shift of 1 km so that the new maximum is 0.175 ppbv at 36.5 km for midlatitudes and we multiply by a scale factor of 0.51 and apply a shift of 2 km so that the new high latitude maximum is 0.100 ppbv at 37.5 km.

3.4 COClF

The retrieval of COClF has not yet been attempted from ACE-FTS measurements. COClF is a reservoir species that results from the breakdown of CCl_3F. *Zander et al.* [1996] used modeled COClF by *Kaye et al.* [1991] for the ATMOS chlorine budget since it makes a significant contribution at high altitudes. The production of COClF modeled by *Kaye et al.* [1991] is based on the thermodynamic assumption that in CFCs, all C-Cl bonds break before C-F bonds and for HCFCs, C-H bonds break first, followed by C-Cl bonds, then C-F bonds. This implies that CCl_2F_2 will breakdown to form COF_2 and that CCl_3F will breakdown to form COClF as follows:

$$CCl_3F + h\nu \rightarrow CCl_2F + Cl \qquad (6.1)$$
$$CCl_2F + O_2 + M \rightarrow CCl_2FO_2 + M \qquad (6.2)$$
$$CCl_2FO_2 + NO \rightarrow CCl_2FO + NO_2 \qquad (6.3)$$
$$CCl_2FO + O_2 \rightarrow COClF + ClOO \qquad (6.4)$$
$$COClF + h\nu \rightarrow Cl + COF \qquad (6.5)$$

The removal of COClF by $O(^1D)$ was also accounted for in the work by *Kaye et al.* [1991] as they modeled COClF at a range of latitudes and different times of the year in 1989.

Figure 1 of *Kaye et al.* [1991] showed that COClF is distributed relatively symmetrically about the equator, although it peaks at lower altitudes and lower VMRs at higher latitudes. Figure 2 of *Kaye et al.* [1991] shows that these Gaussian-like profiles should peak at 0.10 ppbv near 25.5 km in the tropics, decreasing to zero at 10.5 and 34.5 km, peak at 0.04 ppbv near 22.5 km at midlatitudes then decrease to zero at 10.5 and 31.5 km, and peak at 0.02 ppbv near 19.5 km at high latitudes decreasing zero at 10.5 and 28.5. Only a very small seasonal variation was found for COClF in their work.

Although the average of four sources in the WMO report indicates that CFC-11 (CCl_3F) is decreasing at 1.4 pptv per year or 0.53% per year relative to 1996 [*WMO*, 2003, *p 1.8*], Figure 1-1 of the report shows that 1989 and 2004 are within ~2% since they are on opposite sides of the maximum value. The ACE-FTS measured 2004 value is about 247 pptv which is comparable to the value of ~250 ppt for 1989 in Figure 1-1 and a value of 253.3 pptv is given for January 2004 at the earth's surface [*WMO*, 2003, *Table 1-16*]. Since the 2004 values of CCl_3F resemble the 1989 values, it is not necessary to scale the COClF profiles for changes in

CCl_3F over time and we simply incorporate the latitudinally appropriate COClF from the *Kaye et al.* [1991] model into our chlorine budgets.

3.5 $COCl_2$

The retrieval of phosgene ($COCl_2$) from ACE-FTS spectra has not yet been attempted. It is very difficult to retrieve because its spectral lines are buried in the stronger spectrum of CCl_3F. $COCl_2$ was not included in the chlorine budgets based on ATMOS [*Zander et al.*, 1992, 1996] or MkIV measurements [*Sen et al.*, 1999], however, it has since been successfully retrieved from MkIV balloon-borne infrared solar occultation spectra by *Toon et al.*, [2001]. We drew a line of best fit through the MkIV points in the top panel of Figure 2 in *Toon et al.* [2001] for the 6-30 km range. These measurements were made between September 1992 and March 2000, and since the tropospheric levels of the main $COCl_2$ source gases, CCl_4 and CH_3CCl_3, peaked in 1990 and 1992 respectively [*WMO*, 2003], we expect the stratospheric peak in $COCl_2$ to have occurred a few years later, likely near the end of their measurement period. The $COCl_2$ profile was included directly (without scaling or shifting) in each of the five latitude ranges since no clear latitudinal shift can be determined from the data, only a very small temporal change would be expected from this species which makes only a very minor contribution to total stratospheric chlorine (a maximum of ~0.065 ppbv Cl at 20 km).

3.6 $CHClF_2$ (HCFC-22)

The ATMOS and MkIV chlorine budgets [*Zander et al.*, 1992, 1996; *Sen et al.*, 1999] did not include $CHClF_2$ in the upper stratosphere, however, according to *Weisenstein et al.* [1992], $CHClF_2$ has a stratospheric lifetime of 213 years, making it the only organic chlorine species known to exist in the upper stratosphere in significant quantities. Their modeled value in the upper stratosphere was based on the surface value in 1985, but in a more recent work by *Coheur et al.* [2003], a profile of $CHClF_2$ is determined with the global three dimensional chemical transport model SCTM-1 [*Rummukainen et al.*, 1996]. The SCTM-1 model output for 1 January 2000, 00:00 UT, 45ºN, 90ºE is shown in Figure 2. We scaled this profile by a factor of 1.062 based on a comparison of our average midlatitude measured value of $CHClF_2$ in 2004 and their modeled value from 2000 at 19.5 km. The profile was very similar to (yet much smoother than) our northern and southern midlatitude profiles over the 17.5-24.5 km range. This scaled profile was grafted onto both of our midlatitude profiles above the range of ACE-FTS retrievals (beginning at 25.5 km). For northern high latitudes, we shifted the scaled profile down by 5 km before grafting it to the ACE-FTS measurements. We rationalize the need for this shift as a result of descent in the winter Arctic vortex [*Nassar et al*, 2005b] contributing to the annual average profile for northern high latitudes. The southern high latitude profile showed much more descent than the north so it was necessary to shift it down by 10 km to coincide with the ACE-FTS measurements. Similarly, we needed to shift the tropical profile upwards by 10 km to coincide with our measurements. These ACE-FTS profiles and the scaled and shifted SCTM-1 profiles are shown in Figure 2. The application of shifts to the $CHClF_2$ profiles depending on their latitude is qualitatively consistent with the latitudinal distribution of $CHClF_2$ in 1985 modeled by *Weisenstein et al*. [1992], although their model results showed a more symmetrical relationship between the northern and

southern hemispheres (we attribute the lack of hemispheric symmetry in our high latitude profiles to the poor seasonal coverage obtained at high latitudes by including only local sunsets).

3.7 CH_3CCl_3 and minor CFCs, HCFCs, and Halons

The shape of the profile for methylchloroform (CH_3CCl_3) shown in *Zander et al.* [1992, 1996] derived from in situ measurements resembled the averaged ATMOS CCl_4 profiles. Therefore, CH_3CCl_3 and a combination of nine other minor species were calculated using predicted 2004 tropospheric values from the *WMO Report* [2003], applied as a scaling factor to the average ACE-FTS retrieved 2004 CCl_4 profile in each latitude range. Since the WMO predicted surface value of CH_3CCl_3 in 2004 was 0.0275 ppbv [*WMO*, 2003, (*Table 1-16)*], the CCl_4 profile in each latitude range (~0.108 ppbv at midlatitude low altitudes) was scaled by a factor of 0.255 to approximate the profile of CH_3CCl_3. Since CH_3CCl_3 decreases rapidly with altitude in the stratosphere, it is only about 0.003 ppbv by 21.5 km, contributing less than 0.010 ppbv to total chlorine at that altitude.

A combined profile was created for the chlorine contribution from nine other long-lived minor species (including four CFCs, four HCFCs and one halon) listed in Tables 1-1 and 1-16 in the *WMO Report* [2003] with the values summarized in Table 3. The total chlorine contribution near the surface from these species is estimated to be 0.0984 ppbv. A single profile (in each latitude range) was added to account for these nine species by scaling the CCl_4 profile by 0.91. The minor species contribute a maximum of about 2.7% to total chlorine at the surface and decrease rapidly to about 1% (0.036 ppbv) at 18.5 km in the midlatitude lower stratosphere, so errors in their estimation will have a negligible effect on stratospheric Cl_{TOT}.

3.8 ClOOCl

The ClO dimer (ClOOCl) only occurs in significant quantities in the polar vortices, where it exists in equilibrium with ClO. To our knowledge, remote measurements of ClOOCl have never been made, although *Stimpfle et al.* [2004] have made in situ measurements in the Arctic vortex from a NASA ER-2 aircraft during the SOLVE/THESEO-2000 campaign. More recently, *von Hobe et al.* [2005] made in situ aircraft measurements during the SOLVE II/VINTERSOL-EUPLEX and ENVISAT validation campaigns using the HALOX instrument. The measurements by *Stimpfle et al.* [2004] confirm our understanding of the basic mechanism for loss and production of ClOOCl (equations 7.1-7.3) but indicate some uncertainty in the rate constants.

$$ClO + ClO + M \xrightarrow{k^{prod}} ClOOCl + M \qquad (7.1)$$

$$ClOOCl \xrightarrow{j} ClO + ClO \qquad (7.2)$$

$$ClOOCl + M \xrightarrow{k^{loss}} ClO + ClO + M \qquad (7.3)$$

Using these reactions and solving the rate law, a relationship for the expected ClOOCl profile can be determined from the profile of ClO and the appropriate values of the rate constants for

ClOOCl production (k^{prod}), loss by thermal decomposition (k^{loss}) and loss by photolytic decomposition (j).

$$\frac{d[ClOOCl]}{dt} = k^{prod}[ClO]^2[M] - j[ClOOCl] - k^{loss}[M][ClOOCl] = 0 \quad (8.1)$$

$$k^{prod}[ClO]^2[M] = (j + k^{loss}[M])[ClOOCl] \quad (8.2)$$

$$K_{eq} = \frac{[ClOOCl]}{[ClO]^2} = \frac{k^{prod}[M]}{j+k^{loss}[M]} \quad (8.3)$$

Stimpfle et al. [2004] recommend combinations of the above three rate constants that give results consistent with their observations. The value of the photolysis rate constant (j) that we use is the value determined in *Stimpfle et al.* [2004] based on cross sections determined by *Burkholder et al.* [1990] shown in Figure 2a of *Stimpfle et al.* [2004] as a function of solar zenith angle (SZA). Since all ACE-FTS measurements occur at a SZA of 90º, we use a value of $j = 4.4 \times 10^{-4}$ s^{-1} at a SZA = 90º. k^{loss} is determined from the empirical equation $k^{loss}(T) = 9.81 \times 10^{-7} \exp(-7980/T)$ molecules^{-1} cm^3 s^{-1} from *Nickolaisen et al.* [1994] and $k^{prod}(T) = 1.49 \times 10^{-32} (T/300)^{-4.50}$ molecules^{-2} cm^6 s^{-1} from *Bloss et al.* [2001]. (The uncertainties for both rate constants have been ignored in our approximation of the ClOOCl concentration.)

Using the above rate constants, we calculate the ratio $k^{prod}[M]/(j + k^{loss}[M])$ using ACE-FTS retrieved values of temperature and density for each high latitude profile. Since our individual ClO profiles tend to be noisy, we apply the ratio of constants for each profile to the averaged ClO profile to calculate ClOOCl profiles. From the individual ClOOCl profiles, an average profile is calculated over the altitude range of 12.5-26.5 km where ClO enhancement is observed at high latitudes in each hemisphere.

4. Results

The results shown in Figure 3 indicate that total chlorine is nearly constant throughout the stratosphere. In *Zander et al.* [1996] they determined mean Cl_{TOT} by averaging all points in the 16.4-50.2 km altitude range which was intended to span the stratosphere for the northern midlatitudes or subtropics in November. Since the positions of the tropopause and stratopause exhibit seasonal and latitudinal variations, we have used retrieved temperature profiles to determine the altitude of the tropopause and stratopause and by extension the appropriate altitude range to include in our Cl_{TOT} averages. For the purpose of this work, the temperature minimum is used to define the tropopause rather than the lapse rate definition of the tropopause recommended by the WMO, since this would place the tropopause at very low altitudes (~6-8 km) during the polar winters. For all latitude ranges except southern high latitudes, there was a temperature minimum (tropopause) at either 17.5 or 18.5 km and a temperature maximum (stratopause) between 49.5 and 51.5 km altitude. For southern high latitudes, the temperature minimum and maximum occurred at 16.5 and 46.5 km respectively, which is already significantly lower than at other latitudes which will have an effect on comparisons. Based on the tropopause and stratopause positions, we chose to average points in the 17.5 to 50.5 km range to obtain Cl_{TOT} for each latitude range. While this may be a few kilometers high for the southern high latitudes, it helped to avoid the deviation from linearity

which is large below 16.5 km. ACE-FTS stratospheric Cl_{TOT} values for 2004 are shown in Tables 4 and the mean Cl_{TOT} values are shown in Table 5. The method of error determination used by *Zander et al.* [1996] based on the standard deviation of points over a given altitude range was adopted here and should give a reasonable estimate of the precision of mean Cl_{TOT}. Propagating the uncertainty on each species to obtain the uncertainty on total chlorine would largely overestimate the overall uncertainty because the variability in any given species is mostly a result of conversion to another species. Furthermore, it is difficult to make accurate estimates of the uncertainty for the modeled data.

The missing chlorine indicated by the deviation from linearity in the Cl_{TOT} profile between about 15 and 21 km for southern high latitudes may be the result of some chlorine dissolved or frozen in PSCs, since the ACE-FTS only measures species in the gas phase. This is a very likely explanation for the south polar region, but it has not been verified quantitatively. Some portion of the low altitude deviation may also result from our calculated value of ClOOCl, either due to the amplification of errors in ClO affecting the ClOOCl value or errors in the rate constants. Although we have used the values of these rate constants as suggested by *Stimpfle et al.* [2004] which give ClOOCl values that compare well with in situ measurements, *Von Hobe et al.* [2005], *Berthet et al.* [2005] and *Boakes et al.* [2005] all show that the correct values for these rate constants and the resulting equilibrium constant are still the subject of debate. The revised value of K_{eq} suggested by *Boakes et al.* [2005] indicates that ClOOCl may be more abundant than prior studies suggest, which would reduce the deviation from linearity in our southern hemisphere high latitude Cl_{TOT} profile. Smaller deviations from a straight line in both high latitude total chlorine profiles may be related to species such as Cl, Cl_2, and OClO which have not been included in the chlorine budget but make a small contribution at these latitudes. For example, daytime OClO can contribute approximately 0.010 ppbv [*Canty et al.*, 2005] to Cl_{TOT} at certain altitudes.

A principal improvement of the present global budget with respect to most earlier studies is that the ACE-FTS measures a large number of species relative to other satellite instruments but also has better global coverage, better altitude coverage and better vertical resolution than ground based measurements can provide. However, the small number of measurements per day relative to other observation techniques is a significant disadvantage of solar occultation measurements. ACE is often lacking measurements in a particular latitude range for periods of one month or more. In this work, roughly fifty percent of measurements were also neglected since only those at local sunset were included to avoid averaging over diurnal variability. The poor seasonal distribution of ACE profiles used at some latitudes means that ACE and SMR coincidences do not occur frequently enough to properly match profile by profile. Annually averaged ACE-FTS profiles have simply been matched with those of SMR (which obtains better seasonal and global coverage), except at southern high latitudes, where only profiles from the same time period were used so that ClO and HCl would be properly anti-correlated with respect to seasonal variability.

In the lower stratosphere where CCl_4 is still present, our approach of adding a CH_3CCl_3 profile and a profile representing a combination of minor species by scaling the CCl_4 profile is important for obtaining a realistic value for Cl_{TOT}. However, any errors in the retrieved CCl_4 profile are amplified by a factor of eight since the profile shape accounts for a total of eight

chlorine atoms in the Cl_{TOT} calculation, which may also account for some of the non-linearity observed in the lower stratosphere at all latitudes.

If the points in the 17.5-50.5 km altitude range are fit to a straight line, in all cases, they yield a slight positive slope in ppbv/km. These slopes and the associated 1σ standard error on each slope are shown in Table 5. We attribute these slopes to the "age of the air", with a higher value of total chlorine in older air at higher altitudes indicating that the lower stratospheric peak in total chlorine has already past. This result is qualitatively consistent with the lowest total chlorine values occurring in the tropics and the highest at high latitudes due to the Brewer-Dobson circulation. Furthermore, we determined the slope in the Cl_{TOT} profiles in *Zander et al.* [1996] which were measured in 1994 prior to the peak in total stratospheric chlorine. Their data gave a slope of -0.0050 ppbv/km for northern midlatitudes (35-49ºN) and -0.0027 ppbv/km for the northern subtropics (20-35ºN). The negative slopes indicate more chlorine at lower altitudes, which is qualitatively consistent with higher Cl_{TOT} propagating upward in the stratosphere at that time. (The slope from the 1985 chlorine budget [*Zander et al.*,1992] was 0.0038 ppbv/km but in that paper they question its validity, so it is given no further consideration here.)

As mentioned in the introduction, using ground-based measurements, *Mahieu et al.* [2004] determined the post-peak rate of change in Cl_{TOT} to be -0.7%±0.3%/year which would be 0.025±0.011 ppbv/year using 3.6 ppbv as the total value. Assuming a typical lag time of 6.0 years for transport from the surface to 55 km [*Waugh et al.*, 2001], this translates to an average upward propagation of 9.17 km/year. With these assumptions, the decrease in stratospheric chlorine observed should produce a mean slope of 0.00275 ppbv/km. *Zander et al.* [1996] found that Cl_{TOT} was increasing at 0.10 ppbv/year between 1985 and 1994 (assuming a linear increase) which should result in a slope of -0.0109 ppbv/km assuming the same rate of upward propagation. Our midlatitude and tropical slopes range from 2.9-3.3 times larger than the predicted slopes, but at high latitudes, errors in the lower stratosphere have artificially increased the slope. The 1994 ATMOS midlatitude slope is a factor of 2.2 less than the predicted value and their subtropical slope is a factor of 4.0 less. For both the ACE-FTS and ATMOS slopes, slightly better agreement could be obtained if a longer lag time were applied which may be theoretically justified, especially for higher latitudes due to Brewer-Dobson circulation which has been ignored in this first-order calculation. *Neu and Plumb* [1999] modeled the transport of air in a "leaky pipe" model and found that while the mean age difference between midlatitude and tropical air was dependent on the level of horizontal mixing between the tropics and midlatitudes (entrainment parameter, ε), stratospheric midlatitude air was typically 1-2 years older than tropical air of the same altitude. They also state that within the upwelling tropics, the mean age of air increases with height but a relationship is not so clear in the downwelling region of the middle and high latitudes.

5. Discussion

The Earth Observing System Microwave Limb Sounder (EOS-MLS) is a second generation MLS instrument on the NASA Aura satellite that was launched in July 2004 and measures a variety of atmospheric species including HCl. Comparisons have been made between the

EOS-MLS (version 1.5) and ACE-FTS HCl data (version 2.1) by *Froidevaux et al.* [2005]. Based on 623 near-coincident profiles, the agreement between the two instruments was typically much better than 5% from 100 hPa to about 1 hPa (~16-45 km) above which point ACE-FTS values appear about 5-8% higher. More recent comparisons between MLS and ACE-FTS version 2.2 data using 1019 coincident profiles, give a similar result (Figure 4), indicating perhaps even better agreement in the middle and lower stratosphere. *McHugh et al.* [2005] found that ACE-FTS HCl (version 1.0) abundances are 10 to 20% larger than those from HALOE, based on a more limited sampling of 32 coincident profiles, mostly in July 2004. MLS HCl values are also high relative to HALOE by about 0.2 to 0.4 ppbv (~10 to 15%) for roughly the same time period and latitudes used in the ACE-FTS and MLS comparisons [*Froidevaux et al.*, 2005].

The discrepancies between ACE-FTS and MLS HCl are small and comparable to the estimated margin of error on the measurements. The absolute accuracy of HALOE HCl reported by *Russell et al.* [1996b] is 12-24% depending on altitude, so given this wide margin of error, ACE-FTS and MLS results can be considered consistent with those of HALOE. The exact cause of the systematic difference with HALOE is not yet known, but there were early indications that HALOE HCl measurements were low relative to other observations [*Russell et al.*, 1996a, *Russell et al.*, 1996b] as well as evidence from more recent comparisons [*Barret et al.*, 2005]. It is possible that both the ACE-FTS and MLS HCl measurements are slightly high but it is unlikely that they are the sole cause of the large difference with respect to HALOE.

The most important implication of a difference in HCl values is the effect it will have on Cl_{TOT}. We are currently searching for possible causes for the difference between the ACE-FTS and MLS HCl at high altitudes. Since the discrepancy appears limited to pressures above 1 hPa or approximately 45 km at midlatitudes (~48 km in the tropics and ~42 km during the polar winter) this would cause a negligible error in our tropical mean Cl_{TOT} determination, but a small noticeable error at higher latitudes, all of which are based on the 17.5-50.5 km range.

Based on this work as well as *Coheur et al.* [2003] and *Weisenstein et al.* [1992], we estimate that HCl makes up 97-98% of Cl_{TOT} near 55 km altitude, with $CHClF_2$ accounting for about 1% (0.027-0.040 ppbv) and a contribution of less than 0.2% due to other organic chlorine gases. Inorganic chlorine species that may contribute to Cl_{TOT} at this altitude include ClO, HOCl and Cl. We do not have accurate values of the contributions from these species, even for ClO because SMR measurements did not always appear reliable at this altitude, but by our best estimate, the largest contribution (less than 2%) comes from ClO.

The mean Cl_{TOT} values for 2004 obtained in this work by the method of summing stratospheric chlorine species, which range from 3.59 ± 0.11 ppbv for the tropics to 3.71 ± 0.13 ppbv for northern high latitudes are all quite plausible although they are higher than the HALOE value of Cl_{TOT}. When using the method of taking HCl at 55 km to determine the value of Cl_{TOT}, it is rarely emphasized that 55 km is actually in the lower mesosphere not the stratosphere. Therefore, the value obtained can only be used as a direct representation of Cl_{TOT} in the stratosphere if one assumes no slope in the profile. The present work has shown that there is a good theoretical foundation for sloped stratospheric Cl_{TOT} profiles, although the

uncertainty in many of the parameters prevents a more rigorous quantitative treatment. This finding indicates that the slope of the Cl_{TOT} profile coupled with the altitude difference must be considered when comparing HALOE Cl_{TOT} values with ACE-FTS, ATMOS and MkIV values. It also implies that before the peak in upper stratospheric chlorine (~1997), the HALOE 55 km value of Cl_{TOT} should be slightly less than a true stratospheric value and after the peak it should be slightly more, which adds to the discrepancy between ACE-FTS and HALOE Cl_{TOT}.

Waugh et al. [2001] are unable to explain the decline in stratospheric chlorine reported by HALOE which began in 1997 rather than in late 1999 as predicted. According to an update to the HALOE record, after the onset of stratospheric chlorine decline in 1997, a second peak occurred in 2001, at which point it began to decline again [*Anderson and Russell*, 2004] which also remains unexplained. *Waugh et al.* [2001] suggest that the initial early decline in the HALOE calculated value of Cl_{TOT} could be a result of a change to the HCl/Cl_{TOT} ratio due to high altitude organic chlorine species such as HCFC-22, but dismiss this as having too small of an effect. The ACE-FTS and MLS both give systematically higher current values of HCl than HALOE, and past ATMOS and MkIV results also appear higher, even with slope and altitude considerations. Therefore, the unexplained behavior of Cl_{TOT} in the HALOE record may be the result of a combination of true HCl values higher than those reported by HALOE, along with a variable HCl/Cl_{TOT} ratio. We suggest that the ratio may currently be closer to 0.97-0.98 rather than 0.93-0.95, and was actually higher than 0.98 in the past but slowly decreasing as HCFC-22 loading in the stratosphere increases. It may be the case that it is incorrect assumptions about this value that may be responsible for the fluctuation in Cl_{TOT} and the appearance of peaks in 1997 and 2001 rather than a single peak around 1999. However, there are many sources of uncertainty and in the present work, we cannot determine if this hypothesis is quantitatively valid.

6. Summary and Conclusions

We have created an inventory of global stratospheric chlorine including all significant inorganic and organic chlorine species in five latitude ranges during the period of February 2004 - January 2005 inclusive, based on measurements by the ACE-FTS supplemented by measurements by other instruments and model results. The sum of all significant chlorine species at each altitude nearly makes a straight line, with a slight positive slope (ppbv/km) and these points are averaged to determine stratospheric Cl_{TOT} for each latitude range. We obtain a Cl_{TOT} value of 3.59±0.11 ppbv in the tropics, independently obtain 3.62±0.10 ppbv for both the northern and southern midlatitudes, 3.71±0.13 ppbv for northern high latitudes and 3.69±0.17 ppbv for southern high latitudes. Both the latitudinal variation and the slopes can be interpreted as evidence that stratospheric Cl_{TOT} is now declining; however, the slope values are not known accurately enough to obtain quantitative conclusions.

ACE-FTS and MLS HCl measurements agree very well up to 0.1 hPa (or ~45 km altitude), however, comparisons between current ACE-FTS HCl measurements and our calculated values of Cl_{TOT}, MLS HCl measurements, as well as historical ATMOS and MkIV HCl and Cl_{TOT}, all yield higher results than HALOE to varying degrees. However, we can only suggest possible causes for these discrepancies at the current time. Part of the disagreement

between Cl_{TOT} values from the various instruments may be attributed to assumptions about the value of the HCl/Cl_{TOT} ratio. In spite of the higher value of stratospheric chlorine (relative to HALOE) determined in this work, comparing the ACE-FTS result to some historical measurements such as AMTOS and MkIV, indicate that stratospheric Cl_{TOT} has stopped increasing. Furthermore, the slopes from all of our Cl_{TOT} profiles indicate that total chlorine is now steadily declining, reinforcing any previous work that has shown the success of the Montreal Protocol and its amendments at controlling and more recently reducing levels of stratospheric chlorine. However, the result obtained here is significant in the sense that it may take longer for stratospheric chlorine levels to decline to a "safe" level of 2.0 ppbv, than predictions based solely on the HALOE Cl_{TOT} values. If this is the case, it could mean a delay in the expected date of stratospheric ozone recovery by a few years.

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Tables

Table 1: Microwindows for chlorine species retrieved from ACE-FTS measurements.

Species	Retrieved altitude range for average profile (km)	Microwindow		
		Center (cm^{-1})	Width (cm^{-1})	Range (km)
HCl	**8.5 - 56.5**	2701.26	0.3	8.5 - 35.5
		2703.03	0.3	35.5 - 46.5
		2727.77	0.4	8.5 - 44.5
		2751.97	0.3	47.5 - 54.5
		2775.75	0.3	40.5 - 56.5
		2798.95	0.35	51.5 - 56.5
		2819.48	0.3	20.5 - 53.5
		2821.47	0.3	18.5 - 56.5
		2841.63	0.4	20.5 - 49.5
		2843.67	0.3	15.5 - 56.5
		2865.16	0.26	38.5 - 56.5
		2906.30	0.3	45.5 - 56.5
		2923.57	0.5	20.5 - 47.5
		2923.73	0.3	44.5 - 49.5
		2925.90	0.3	17.5 - 56.5
		2942.67	0.4	15.5 - 53.5
		2944.95	0.3	10.5 - 56.5
		2961.00	0.4	25.5 - 47.5
		2963.11	0.5	8.5 - 56.5
		2981.00	0.5	40.5 - 56.5
		2995.88	0.3	45.5 - 50.5
		2998.14	0.3	52.5 - 56.5
$ClONO_2$	**12.5 - 34.5**	780.15	0.6	12.5 - 19.5
		1202.86	0.5	12.5 - 17.5
		1292.60	1.6	18.5 - 34.5
		1728.28	0.5	12.5 - 17.5
ClO*	**12.5 - 24.5**	823.475	5	11.5 - 29.5
		828.475	5	11.5 - 29.5
		833.475	5	11.5 - 29.5
		838.475	5	11.5 - 29.5
		843.475	5	11.5 - 29.5
CH_3Cl	**9.5 - 24.5**	2966.50	0.4	9.5 - 24.5
		2966.90	0.4	9.5 - 24.5
		2967.30	0.7	9.5 - 24.5
CCl_4	**8.5 - 22.5**	799.85	11	8.5 - 22.5

CCl_3F (CFC-11)	**5.5 - 21.5**	842.50	25	5.5 - 21.5
CCl_2F_2 (CFC-12)	**6.5 - 27.5**	922.00	4	6.5 - 27.5
		1161.00	1.2	12.5 - 24.5
$CHClF_2$ (HCFC-22)	**5.5 - 24.5**	809.30	1.1	5.5 - 14.5
		820.85	0.7	5.5 - 11.5
		829.03	0.5	5.5 - 24.5
CCl_2FClF_2 (CFC-113)	**7.5 - 16.5**	817.50	25	7.5 - 16.5
CH_3CClF_2 (HCFC-142b)	**8.5 - 18.5**	1134.50	4	8.5 - 18.5
		1193.60	3.6	8.5 - 18.5

*ACE-FTS ClO retrieval only used for southern high latitudes over a reduced altitude range.

Table 2: Number of profiles averaged for each latitude range.

	Maximum ACE-FTS profiles	**Odin SMR ClO profiles**
Northern high latitudes	63	72
Northern midlatitudes	131	58
Tropics	170	157
Southern midlatitudes	180	22
Southern high latitudes	135	38

Table 3: Minor organic chlorine species included in the chlorine budget based on their predicted values in the *WMO Report* [2003]. Surface VMRs are given in parts per trillion by volume (pptv).

Chemical Formula	**Industrial Name**	**VMR of species**	**VMR contribution to Cl_{TOT}**
$CClF_3$	CFC-13	3.5	3.5
$CClF_2CClF_2$	CFC-114	16.4	32.8
CCl_2FCF_3	CFC-114a	1.8	3.6
$CClF_2CF_3$	CFC-115	9.2	9.2
$CHCl_2F$	HCFC-21	0.29	0.58
$CHCl_2CF_3$	HCFC-123	0.03	0.06
$CHClFCF_3$	HCFC-124	2.7	2.7
CH_3CCl_2F	HCFC-141b	20.9	41.8
$CBrClF_2$	Halon-1211	4.16	4.16
TOTAL			**98.4**

Table 4: Cl_{TOT} as a function of altitude from 17.5 to 50.5 km in five latitude regions.

	Total Chlorine / ppbv				
Altitude / km	**North Polar**	**North Mid**	**Tropics**	**South Mid**	**South Polar**
17.5	3.60	3.54	3.56	3.49	3.30
18.5	3.49	3.49	3.48	3.47	3.30
19.5	3.48	3.48	3.55	3.49	3.42
20.5	3.60	3.54	3.51	3.52	3.40
21.5	3.64	3.52	3.55	3.53	3.48
22.5	3.69	3.52	3.54	3.57	3.61
23.5	3.66	3.54	3.60	3.58	3.60
24.5	3.60	3.53	3.53	3.60	3.67
25.5	3.56	3.50	3.50	3.57	3.66
26.5	3.59	3.53	3.56	3.58	3.68
27.5	3.64	3.57	3.59	3.59	3.68
28.5	3.69	3.60	3.57	3.60	3.67
29.5	3.69	3.62	3.55	3.61	3.65
30.5	3.70	3.62	3.51	3.59	3.63
31.5	3.71	3.59	3.50	3.58	3.62
32.5	3.73	3.59	3.47	3.55	3.63
33.5	3.72	3.56	3.47	3.53	3.63
34.5	3.72	3.56	3.48	3.54	3.63
35.5	3.67	3.56	3.48	3.55	3.66
36.5	3.62	3.53	3.47	3.55	3.69
37.5	3.62	3.54	3.49	3.57	3.72
38.5	3.66	3.60	3.54	3.63	3.76
39.5	3.69	3.64	3.57	3.65	3.79
40.5	3.72	3.68	3.62	3.68	3.81
41.5	3.75	3.70	3.66	3.70	3.82
42.5	3.79	3.70	3.69	3.72	3.84
43.5	3.82	3.70	3.70	3.74	3.85
44.5	3.85	3.71	3.70	3.76	3.87
45.5	3.86	3.73	3.70	3.77	3.89
46.5	3.88	3.75	3.73	3.77	3.88
47.5	3.93	3.76	3.76	3.76	3.88
48.5	3.96	3.79	3.81	3.76	3.88
49.5	3.96	3.82	3.81	3.77	3.88
50.5	3.96	3.83	3.80	3.78	3.88

Table 5: Mean total chlorine with 1σ precision and the slope (ppbv/km) with 1σ standard error for the points from 17.5-50.5 km altitude in five latitude regions.

	Mean Cl_{TOT} (ppbv)	**slope (ppbv/km)**
Northern high latitudes	3.71 ± 0.13	0.011 ± 0.002
Northern midlatitudes	3.62 ± 0.10	0.009 ± 0.002
Tropics	3.59 ± 0.11	0.008 ± 0.002
Southern midlatitudes	3.62 ± 0.10	0.009 ± 0.002
Southern high latitudes	3.69 ± 0.17	0.015 ± 0.003

Figures

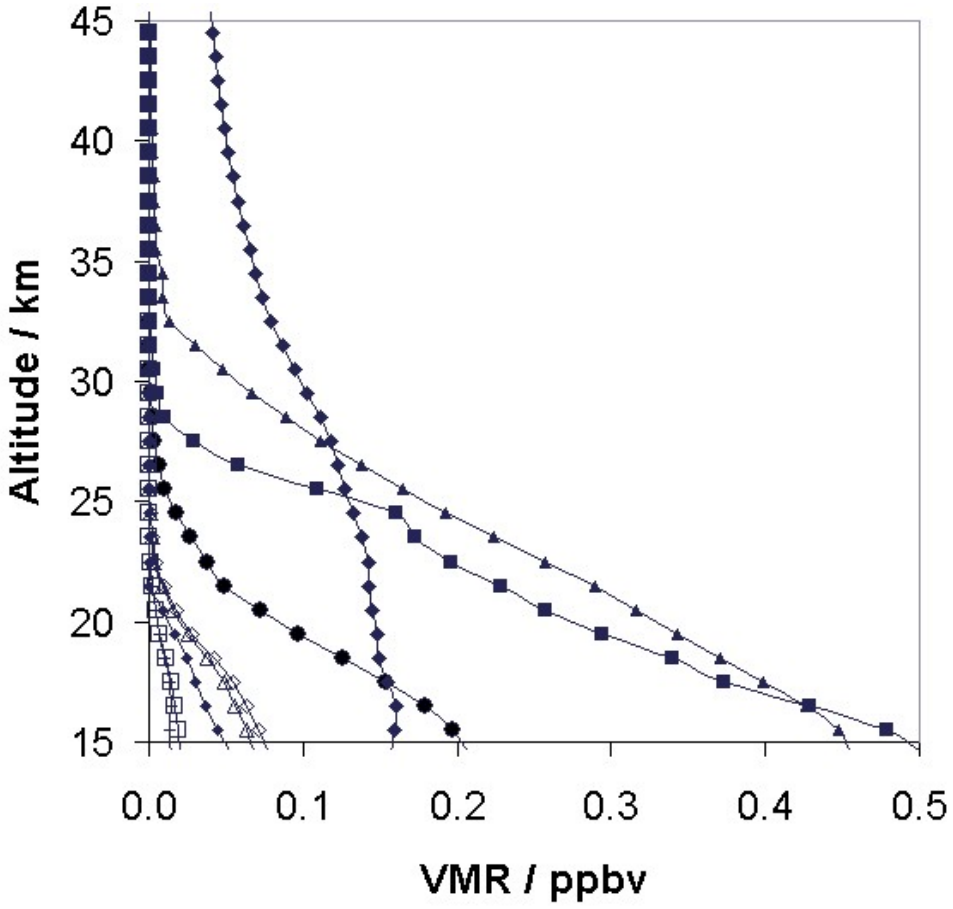

Figure 1: Averaged organic chlorine profiles for southern midlatitudes in 2004: CCl_2F_2 (▲), CCl_3F (●), $CHClF_2$ (◆), CH_3Cl (■), CCl_4 (◇), CH_3CClF_2 (–), CCl_2FCClF_2 (⬥), CH_3CCl_3 (□) and a combination of other minor species (Δ).

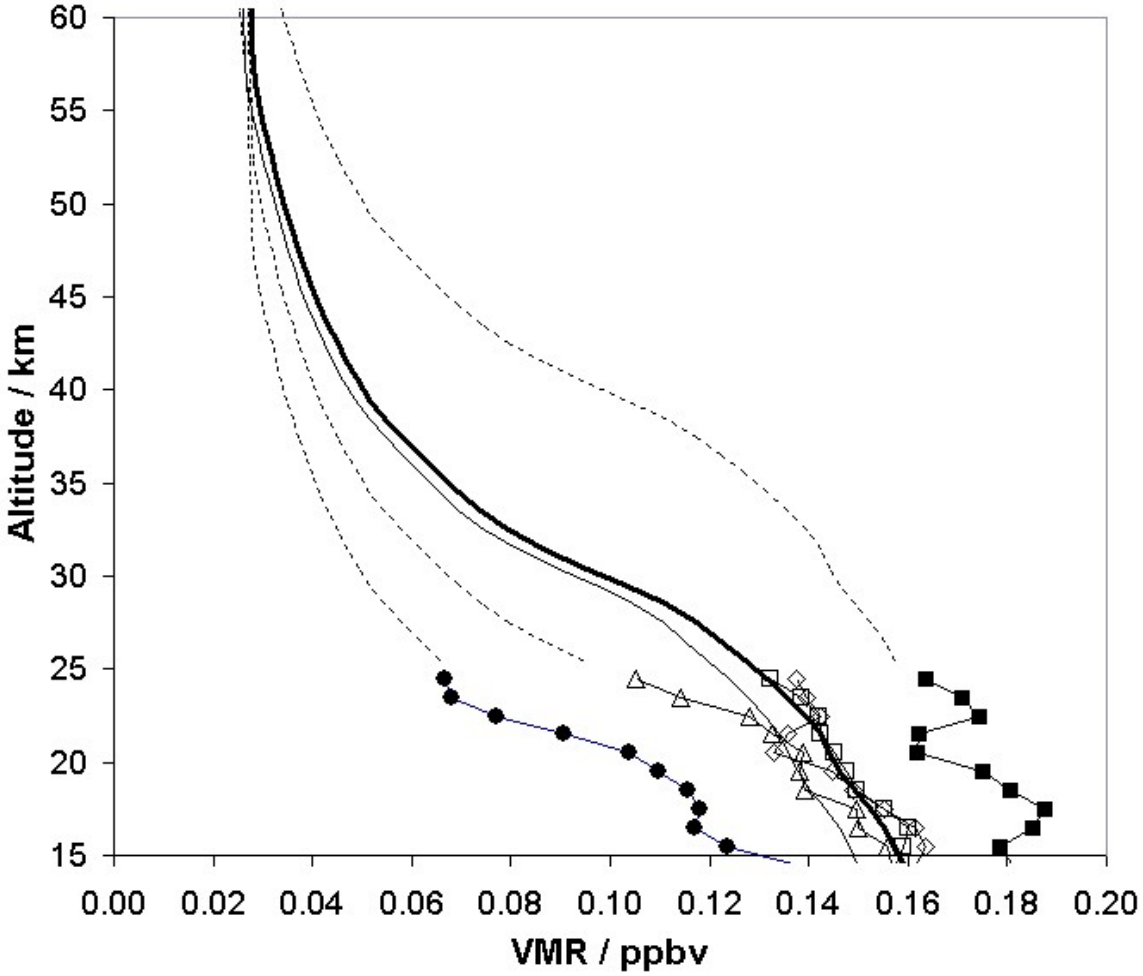

Figure 2: Profiles of $CHClF_2$ (HCFC-22) in the stratosphere: the SCTM-1 modeled profile for 45ºN in 2000 (thin line), the SCTM-1 profile scaled for 2004 (thick line), ACE-FTS measured values in the southern high latitudes (●), southern midlatitudes (□), tropics (■), northern midlatitudes (◇) and northern high latitudes (Δ). The scaled and shifted SCTM-1 profiles for extending the ACE-FTS measurements to higher altitudes are shown as dotted lines.

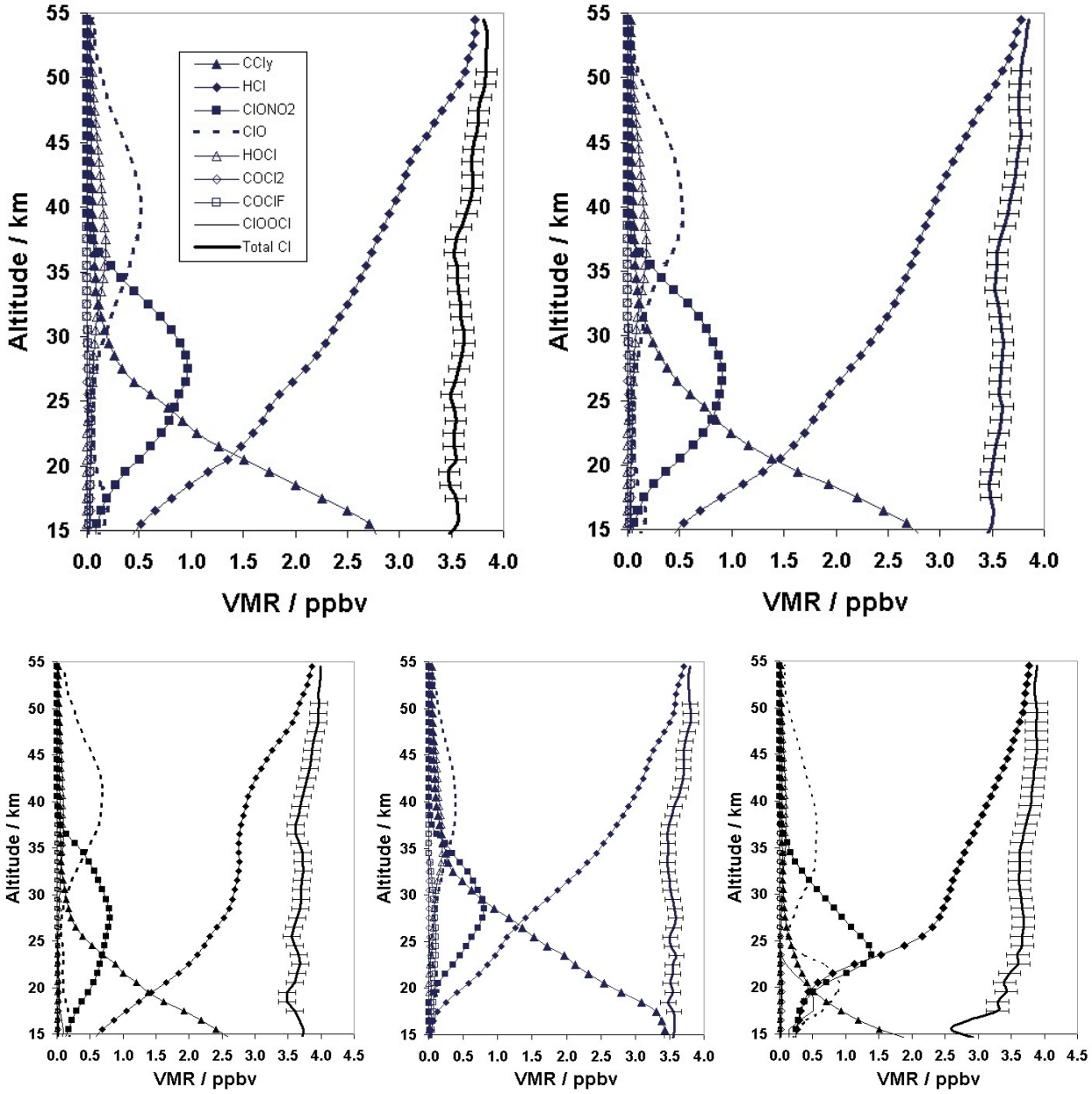

Figure 3: Stratospheric chlorine inventories for 2004: northern midlatitudes (30-60ºN, top left), southern midlatitudes (30-60ºS, top right), northern high latitudes (60-82ºN, bottom left), tropics (30ºS-30ºN, bottom middle), southern high latitudes (60-82ºS, bottom right). Error bars are included on the total chlorine profiles for the 17.5-50.5 km range.

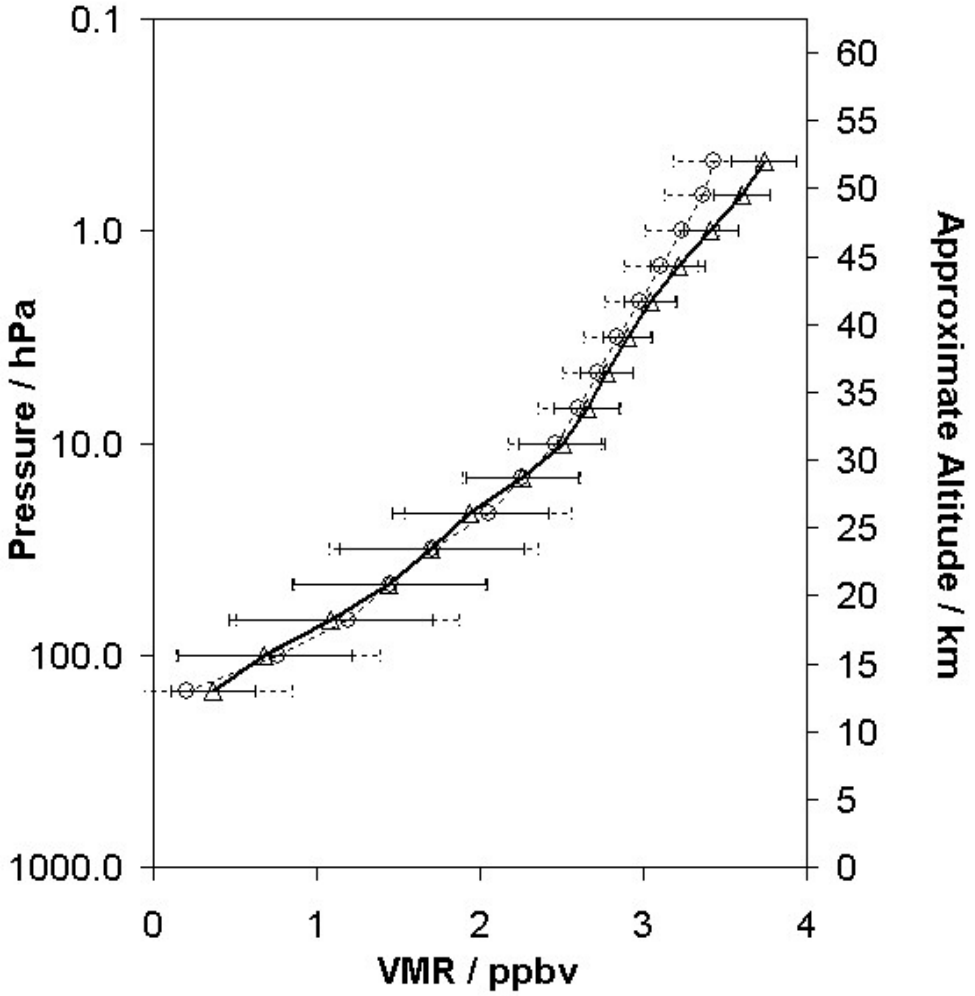

Figure 4: A comparison showing average HCl profiles based on MLS (circles, dotted line) and ACE-FTS (triangles, solid line) coincidences. 1019 coincidences from the period of August 2004 to 31 January 2005 were used, although at the upper and lower ends of the altitude range fewer profiles are included in the average. The criteria for coincidences are measurements within 1° latitude, 8° longitude and 12 hours. This comparison includes both ACE-FTS sunrise and sunset occultations, with all ACE-FTS data interpolated to the MLS vertical pressure grid. The error bars indicate the 1σ variability for each set of data.